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PATENT SPECIFICATION

761,055



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COMPLETE SPECIFICATION

Improvements in Methods and Apparatus for Detecting and Measuring the Concentration of Gases.

I, ARTHUR LIGHT a British subject of 163, Braeside Avenue, Patcham, Brighton, in the County of Sussex, do hereby declare the invention for which I pray that a patent may be granted to me, and the method by which it is performed to be particularly described in and by the following statement:—

It has long been known that the passage of a mixture of oxygen and hydrogen over a palladium catalyst will cause a proportion of the two gases to combine to form water in an exothermic flameless reaction. This fact can be utilised to detect the presence, and/or measure the concentration, of relatively small proportions of one of these two gases in the other gas or in a gaseous mixture comprising the other gas, the gas to be tested being passed over a palladium catalyst and temperature sensitive means provided which respond to the heat that is generated if both gases are present. The gas required for reaction with the gas to be detected may be added for the purposes of the test. For example, in controlling the commercial production of nitrogen, or other inert gas, the gas produced can be tested for the presence of oxygen by injecting hydrogen into a stream of the gas produced and passing this stream over the catalyst.

In the gas detecting and measuring devices operating on the above principle which have previously been used, or proposed for use, the palladium catalyst is supported on granules or pellets of alumina; a stream of the gas to be tested is passed through a mass of these granules or pellets; temperature sensitive elements (for example the hot and cold junctions of a thermopile) are inserted in the gas stream on the entry and exit sides of the catalyst mass and the difference in temperature is observed. Such devices are slow in response, the time required to reach a steady temperature after a change in the concentration of the reacting gas being in practice of the order of 12 minutes. More-

over, the temperature rise observed for a given concentration may vary substantially since any shifting of the granules or pellets will tend to alter the proportion of the reacting gases present which is actually caused to react.

In accordance with the present invention the rise in temperature of the catalyst itself, as distinct from that of the gas stream which has flowed over the catalyst, is observed and/or measured. This is effected by so supporting the catalyst that it is in solid contact with the temperature sensitive device used to detect the heat of reaction, that is to say the catalyst is either in direct contact with the temperature sensitive device or it is in direct contact with a solid support which in turn is in direct contact with the temperature sensitive device. The temperature sensitive element can then be given a small thermal mass, so that the time required to reach a steady state is greatly reduced. Moreover, the presentation of the catalyst to the gas stream does not vary, so that the response to a given concentration of the gas to be detected will remain constant.

It should here be acknowledged that there has previously been proposed an apparatus for detecting the presence of combustible gases or vapours in the atmosphere of mines or other places, which comprises a button on a porous substance having incorporated therein finely divided palladium or other catalyst and a similar button not incorporating any catalyst. The buttons are formed with apertures in which are inserted the two polar junctions of a thermo-electric circuit, which includes electric measuring and alarm devices, and are provided with equal heating means to maintain the catalyst at an efficient temperature. The two buttons are mounted in a screened enclosure so as to be exposed to the atmosphere to be tested, the presence of combustible gases causing a rise in temperature of the button incorporating the

[Price 3s. 0d.]

Price 3s. 6d.

Price 4s. 6d.

Price 25p

catalyst.

The accompanying drawing illustrates somewhat diagrammatically one particular form of apparatus in accordance with the invention.

The apparatus illustrated comprises a tubular chamber 1, thermally insulated by means of an evacuated jacket 2, and provided near its ends with branch pipes 3 and 4, which respectively form an inlet and an outlet for the gas to be tested. A pair of temperature sensitive devices, designated generally by the reference numerals 5 and 6 are inserted through the two ends of the tube. Each of these devices includes a so called thermister of the type comprising a small bead 7 of a complex metal oxide compound having a high negative temperature coefficient of resistance which is formed on two spaced wires and is secured on one face of a copper disc 8. This disc is sealed across the end of a glass tube 9 which projects through the end of the tube 1 and accommodates the lead-in wires 10 to the thermister device. A disc 11 of sintered glass supporting the palladium catalyst is secured to the copper disc 8 of the thermister 6 furthest from the gas inlet. The two thermisters are connected by the lead-in wires in the conjugate arms of a bridge circuit (not shown), which includes means for measuring the current which flows when the balance is disturbed by the rise in the temperature of device 6 over that of device 5 produced by the occurrence of chemical reaction.

The size of the sintered glass disc 11 is selected, in dependence upon the percentage content of reacting gas expected in the gas tested, to produce a convenient degree of temperature difference between the two thermisters. The palladium catalyst may be applied to the disc by saturating it with a solution of palladium chloride and heating to a temperature of about 600°C, thereby evaporating the solution and reducing the salt to leave the palladium in position in finely divided metallic form. The disc can be adhesively secured to the copper disc of the thermister with a cold setting resin adhesive loaded with metallic powder to improve the thermal conductivity between the catalyst and the temperature sensitive device.

The particular form of apparatus described and illustrated has a stabilisation time of only about 2 minutes and allows measurement of concentrations of oxygen or hydrogen down to about 0.1%. If desired, the stabilisation period can be further reduced by employing temperature sensitive devices of lower thermal mass, for example a thermister device having the metal oxide bead provided with a local coating of glass on which the palladium catalyst is deposited. Measurement of concentrations of oxygen

or hydrogen down to about 10 parts per million can be effected by mounting the two temperature sensitive devices in separate thermally insulated chambers (which, together with a gas passage connecting them, are disposed within an outer thermally insulated chamber, to protect them from outside influence) so as to prevent the lower temperature device from being affected by heat from the higher temperature device, and connecting the devices in an alternating current bridge circuit fed from a high stability oscillation generator and provided with an output amplifier.

If the apparatus is required to have a high degree of long term stability, it is preferable to employ platinum resistance thermometers in place of thermister devices as the temperature sensitive elements. In this case a convenient arrangement is to deposit the catalyst on sintered glass forming the wall of a tube through which the gas is caused to flow, one of the platinum resistance wire elements being wound onto the outside of this tube.

Many other modifications of the apparatus particularly described and illustrated are also possible within the scope of the invention, as defined by the appended claims.

What I claim is:—

1. A method of detecting the presence, and/or measuring the concentration, of oxygen or hydrogen in a gas or gaseous mixture consisting of or containing the other of those two gases, according to which a stream of the gas to be tested is caused to flow over a palladium catalyst and any rise in temperature of the catalyst above the temperature of the gas stream flowing towards the catalyst is observed and/or measured.

2. Apparatus for detecting the presence, and/or measuring the concentration, of oxygen or hydrogen in a gas or gaseous mixture consisting of or containing the other of those two gases, comprising a pair of temperature sensitive elements, means for causing a stream of the gas to be tested to flow in succession over those elements, a palladium catalyst exposed to the gas and so supported as to be solid contact (as herein defined) with the second of those elements, and means for detecting and/or measuring any rise in the temperature of the second element above that of the first element.

3. Apparatus in accordance with claim 2 in which the two temperature sensitive elements are mounted in a common, thermally insulated chamber.

4. Apparatus in accordance with claim 2 in which the two temperature sensitive elements are mounted in separate thermally insulated chambers, which together with a gas passage connecting them are enclosed in a common thermally insulated chamber.

5. Apparatus in accordance with any of

claims 2, to 4, in which the temperature sensitive elements are electrically responsive and are connected in the conjugate arms of a bridge circuit including means for measuring the current which flows when the balance is disturbed by the occurrence of a temperature difference between the two elements.

6. Apparatus in accordance with claim 5 in which the temperature sensitive elements are thermister devices.

7. Apparatus in accordance with claim 6 in which the palladium catalyst in finely divided metallic form is supported in a plate of sintered glass adhesively secured to a metal plate forming part of one of the thermister devices.

8. Apparatus in accordance with claim 5, in which the temperature sensitive elements

are platinum resistance thermometers.

9. Apparatus in accordance with claim 8, in which the palladium catalyst in finely divided metallic form is supported in sintered glass forming the wall of a tube through which the gas to be tested flows, one of the platinum resistance elements being wound onto the outside of this tube.

10. Apparatus in accordance with claim 2 and constructed and arranged substantially as herein described and shown in the accompanying drawing.

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PROVISIONAL SPECIFICATION

Improvements in Methods and Apparatus for Detecting and Measuring the Concentration of Gases.

I, ARTHUR LIGHT, a British Subject of 163, Braeside Avenue, Patcham, Brighton, in the County of Sussex, do hereby declare the invention to be described in the following statement:—

It has long been known that the passage of a mixture of oxygen and hydrogen over a palladium catalyst will cause a proportion of the two gases to combine to form water in an exothermic flameless reaction. This fact can be utilised to detect the presence, and/or measure the concentration, of relatively small proportions of one of these two gases in another gas or gaseous mixture, the gas to be tested being passed over a palladium catalyst and temperature sensitive means provided which respond to the heat that is generated if both gases are present. The gas required for reaction with the gas to be detected may be already present as a normal constituent in the gas to be tested, for example when testing air for hydrogen content. Alternatively, it may be added for the purposes of the test; for example when testing nitrogen, or other inert gas, for the presence of oxygen, hydrogen can be injected into the stream of gas passed over the catalyst.

In the gas detecting and measuring devices operating on the above principle which have previously been used, or proposed for use, the palladium catalyst is supported on granules or pellets of alumina; a stream of the gas to be tested is passed through a mass of these granules or pellets; temperature sensitive elements (for example the hot and cold junctions of a thermopile) are inserted in the gas stream on the entry and exit sides of the catalyst mass and the differences in temperature is observed. Such devices are slow in response, the time required to reach a steady

temperature after a change in the concentration of the reacting gas being in practice of the order of 12 minutes. Moreover, the temperature rise observed for a given concentration may vary substantially, since any shifting of the granules or pellets will tend to alter the proportion of the reacting gases present which is actually caused to react.

In accordance with the present invention, the catalyst is supported in direct contact with the temperature sensitive element used to detect the heat of reaction, so that it is the rise in temperature of the catalyst rather than that of the gas stream that is measured. The temperature sensitive element can be given a small thermal mass, so that the time required to reach a steady state is greatly reduced, and the presentation of the catalyst to the gas stream will not vary, so that the response to a given concentration will remain constant.

A particular form of apparatus in accordance with the invention comprises a tubular chamber thermally insulated by means of an evacuated jacket and provided near its ends with branch pipes which form an inlet and an outlet for the gas to be tested. Temperature sensitive electric resistance devices are inserted through the two ends of the tube, the two devices being similar except that at the exit end is provided with a coating of the catalyst. The two resistance elements are connected in the conjugate arms of a bridge circuit, including means for measuring the current which flows when the balance is disturbed by the temperature change produced by the occurrence of chemical reaction.

The two temperature sensitive devices used in this apparatus are so-called thermisters of the type comprising a small bead of a com-

plex metal oxide compound having a high negative temperature coefficient of resistance, which is formed on two spaced wires and is sealed into the thickness of the wall at the tip of a glass tube, through which the lead wires extend. A deposit of palladium on one of these devices may conveniently be produced by coating the tip of the glass tube with adhesive, dipping it into palladium chloride in powder form and heating to a temperature of about 600°C to reduce the palladium to metallic form. However, the deposit may be produced in other ways, for example by sputtering, or by adhesively attaching metallic palladium.

The particular form of apparatus last described has a stabilisation time of only about 2 minutes and this time could be further reduced by employing a thermister device of lower thermal mass, as by giving the bead only a local coating of glass instead of embedding it in the wall of a glass tube. The apparatus as described allows measure-

ment of concentrations of oxygen or hydrogen down to about 0.1% and still smaller concentrations could be measured by suitable modification of design.

It will be understood that the description of a particular form of apparatus is given by way of example only and that many alternative arrangements are possible. Thus, instead of supporting the palladium directly upon the temperature sensitive element, palladium supported on a base may be mounted in thermal contact with the element. For example, finely divided palladium may be mixed with a binder and the mass moulded into the form of a sheath which is applied over the element.

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761,055
1 SHEET

COMPLETE SPECIFICATION

*This drawing is a reproduction of
the Original on a reduced scale.*



